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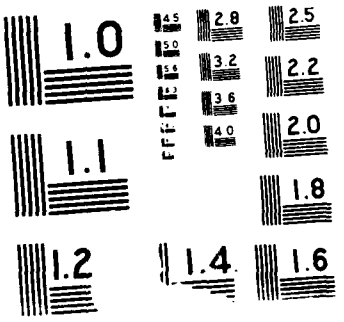
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CORRELATIONS BETWEEN WETTABILITY AND STRUCTURE IN MONOLAYERS OF ALKANETHIOLS ADSORBED ON GOLD

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Correlations between Wettability and Structure in Monolayers of Alkanethiols Adsorbed on Gold[1]

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Abstract

Long-chain alkanethiols adsorb onto gold from solution and form monolayers. Coadsorption of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{21}CH_3$ from ethanolic solutions of varying composition generates monolayers, the wettability of which is correlated closely with the composition of the monolayer. Adsorption of the longer-chain thiol is preferred over the short chain, and formation of monolayers comprising predominantly one component is favored over mixed monolayers containing both component thiols.

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Long-chain thiols ($HS(CH_2)_nX$) adsorb from solution onto gold surfaces and form well-packed, ordered, oriented monolayers.[3,4] The sulfur coordinates strongly to the gold, the polymethylene chains are all-trans and tilted ~20–30° from the normal to the surface,[4,5] and the tail group, X, is the predominant group exposed at the monolayer/liquid or monolayer/air interface.[6] Coadsorption of two or more thiols differing in tail group or chain length provides a flexible system for varying the chemistry and structure of the surface in a controlled and pre-determined way.[7] In this paper we use monolayers comprising a mixture of $HS(CH_2)_{11}OH$ (represented as $HSC_{10}CH_2OH$ to emphasize the two important variables: chain length and tail group) and $HS(CH_2)_{21}CH_3$ ($HSC_{21}CH_3$) on gold to demonstrate a relationship between the microscopic structure of the surface and the wettability of the monolayer (Figure 1). This work is part of a program of physical-organic chemistry designed to relate atomic-level structure of a surface to macroscopic physical properties such as wetting and adhesion.[8]

Monolayers were formed by immersing gold-mirror substrates (prepared by evaporation of gold onto chromium-primed, polished silicon wafers) in solutions of the thiols in degassed ethanol for 12 hours[9] at room temperature.[6] The composition of the monolayer was controlled by varying the ratio $R = [HSC_{10}CH_2OH]/[HSC_{21}CH_3]$ in *solution*, with the total concentration of thiols held constant at 1 mM. We used two independent techniques, optical ellipsometry and X-ray photoelectron spectroscopy (XPS), to measure the composition of the monolayer. Since the two thiols differ in chain length, the relative thickness obtained from ellipsometry and from the peak area of gold[10] in XPS reflects this composition. Similarly, the difference in tail groups allows us to calculate the surface concentration of $HSC_{10}CH_2OH$ from the peak area of oxygen. The advancing contact angles (θ_a) of water and hexadecane (HD) provide useful measures of wettability. Since the pure methyl-terminated monolayer is hydrophobic ($\theta_a(H_20) = 114°$, $\theta_a(HD) = 48°$), and the alcohol-terminated monolayer is hydrophilic ($\theta_a(H_20) = \theta_a(HD) \approx 0°$),

contact angles are very sensitive to the composition of the monolayer and the structure of the surface.

Figure 2 plots the ellipsometric thickness, contact angles of water and hexadecane, and XPS peak areas of gold and oxygen against R.[11] Here we note two salient features of these graphs: a detailed discussion will be deferred to a subsequent paper. First, ellipsometry and XPS peak areas indicate a dramatic change in the composition of the monolayer over a narrow range of solution composition, R = 7 - 20. This change in the composition of the monolayer is closely correlated with a sharp increase in the hydrophilicity and oleophilicity of the surface as measured by the advancing contact angles of water and hexadecane, respectively.[12] Thus the structure of the surface on a microscopic scale is clearly and directly linked to the wettability of the monolayer, an important macroscopic quantity. Second, the inflection in the curves occurs, not at R = 1, but at R ≈ 11.[13,14] This difference between solution and surface compositions is a general feature of competitive adsorption experiments.[15] In this experiment, Van der Waals forces between close-packed hydrocarbon chains favour adsorption of the longer-chain thiol.

We attempted to model the composition of the monolayer by a simple equilibrium expression (Eq. 1) between the solution and the surface (dotted curve in Figure 2, upper graph)

$$HSC_{10}CH_2OH_{surface} + HSC_{21}CH_{3solution} \rightleftharpoons HSC_{10}CH_2OH_{solution} + HSC_{21}CH_{3surface} \qquad (1)$$

where the equilibrium constant $K_{eq} = 11$, *independent* of solution concentration. Clearly the observed data do not follow this simple expression: the two components of the monolayer do not act independently, and may act cooperatively to minimize the free energy. Monolayers composed predominantly of the long-chain methyl-terminated thiol $HSC_{21}CH_3$ (maximizing the chain-packing interactions) or the short-chain hydroxy-terminated thiol $HSC_{10}CH_2OH$ (maximizing H-bonding both with the solvent and within the monolayer)

are preferred over monolayers containing a mixture of the thiols.[16] The data do not, however, take the form of step functions in R, which would be expected thermodynamically if the formation of macroscopic islands were favored.[17] Over a narrow range of R it is possible to form intermediate monolayers containing both thiols; the exact structure of these monolayers is not clear, but the data are consistent with a model in which the two components segregate into small clusters on the surface. These monolayers provide a model system for studying the wettability of complex structures, and for examining how polar groups interact to minimize their energy in a non-polar environment.[18]

Mixed monolayers of thiols on gold allow us to engineer ordered, two-dimensional systems with Å--level control over thickness and structure, and with chemical control over wettability. Synthetic variation of the tail groups and chain lengths provides great flexibility in the design of the interfacial structures and gives these systems wide applicability in the physical, biological and medical sciences.

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References and Notes

[1] Supported in part by the Office of Naval Research and the Defense Advanced Projects Research Agency. XPS spectra were obtained using facilities obtained through the DARPA/URI and maintained in the Harvard University Materials Research Laboratory.

[2] IBM Pre-Doctoral Fellow in Physical Chemistry 1985-86.

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[9] For pure thiols, initial monolayer formation is very rapid (~few seconds) with limiting properties reached after a few hours.

[10] The intensity of the photoelectron peak decreases exponentially with the thickness of the monolayer due to inelastic scattering of the photoelectrons (Briggs, D.; Seah, M. P *Practical Surface Analysis*; Wiley: Chichester, 1983).

[11] We prefer logR to the mole fraction, χ, as the abscissa because kTlogR is related to the Gibbs free energy and hence this choice of axis highlights thermodynamic contributions to the adsorption process.

[12] Hexadecane and water interact predominantly by dispersion and polar forces, respectively. The detailed inferences from the contact angle data and comparisons with other monolayer systems will be discussed in a subsequent paper.

[13] The ellipsometric thickness yields a value of $R(\chi_{1/2}) = 11$ where $\chi_{1/2}$ = 1:1 ratio of the two thiols in the monolayer. XPS peak areas yield $R(\chi_{1/2})$ = 10–12 depending on the model used to analyze the data.

[14] The monolayer system had not quite reached equilibrium when these measurements were made. Over a period of two weeks $R(\chi_{1/2})$ slowly increased to R ≈ 14.

[15] Bain, C. D.; Whitesides, G. M. unpublished results.

[16] Despite being enthalpically disfavored, some $HSC_{21}CH_3$ is incorporated into the $HSC_{10}CH_2OH$ monolayer even at large R (and vice versa) due to the favorable entropy of mixing.

[17] We believe that adsorption of thiols onto gold is controlled to a large extent by thermodynamics, although kinetics also play a role, as evinced by the slow change in the monolayer composition with time after the initial, rapid adsorption.

[18] Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic: New York, 1985.

FIGURE CAPTIONS

Figure 1. Schematic illustrations of monolayer structures: pure $HS(CH_2)_{11}OH$ (A); pure $HS(CH_2)_{21}CH_3$ (B); monolayer containing a mixture of the two thiols (C).

Figure 2. Monolayers formed by the adsorption of mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{21}CH_3$ onto gold from solution. The abscissa represents the ratio, R = $[HS(CH_2)_{11}OH]/[HS(CH_2)_{21}CH_3]$ in *solution*. Squares and circles represent data from two separate experiments. Upper Figure: ellipsometric thickness. The solid curve is a fit to the data. The dotted curve represents the theoretical thicknesses for $K_{eq} = 11$ (see text for definition). Middle Figure: advancing contact angles of water (open symbols) and hexadecane (HD) (solid symbols) obtained by the sessile drop technique. Lower Figure: areas of the Au $4f^7/_2$ (open symbols) and O 1s peaks (solid symbols) obtained by XPS. The vertical scale is arbitrary. Data were collected on a SSX-100 X-ray photoelectron spectrometer (Surface Science Instruments) with a monochromatized Al Kα source, 100 eV pass energy, and 1–mm X-ray spot. The peaks were fitted using a symmetrical 90% Gaussian/ 10% Lorentzian profile.

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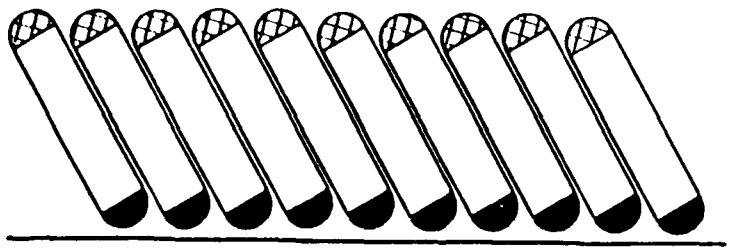

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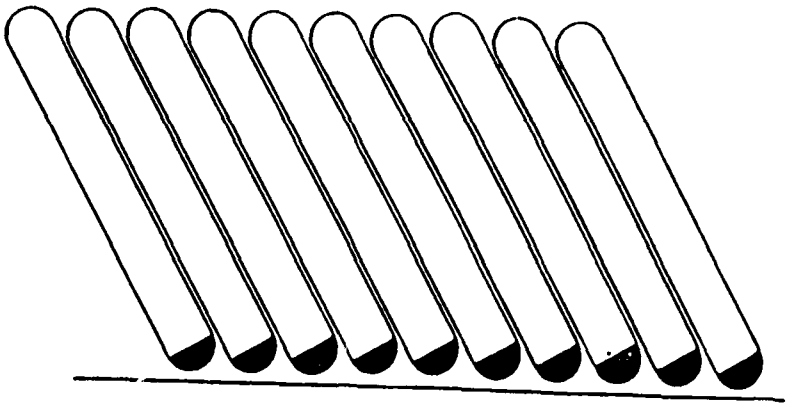

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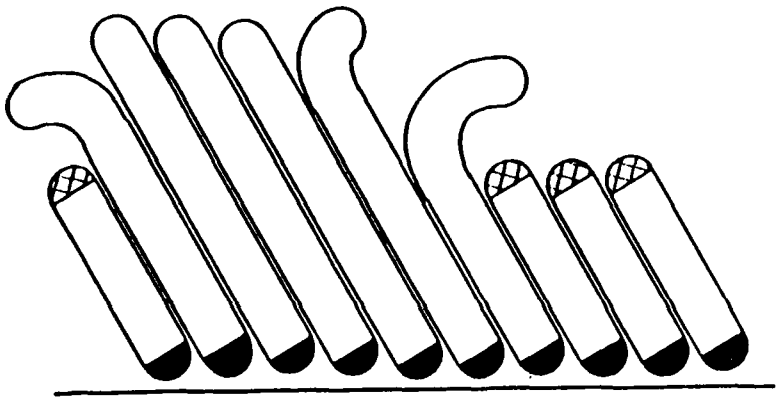

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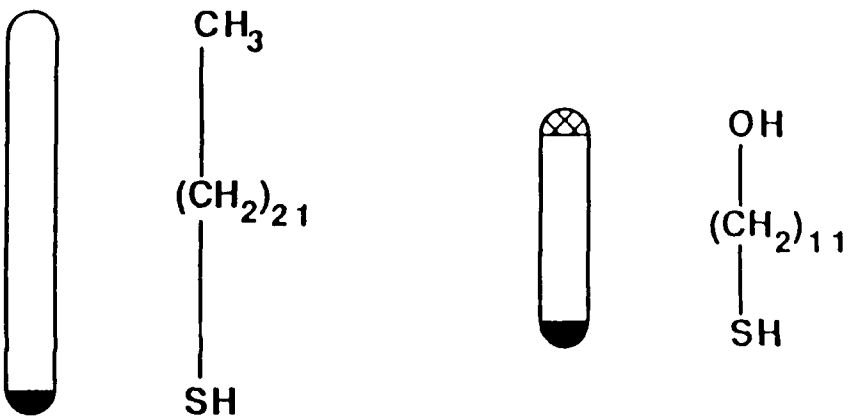

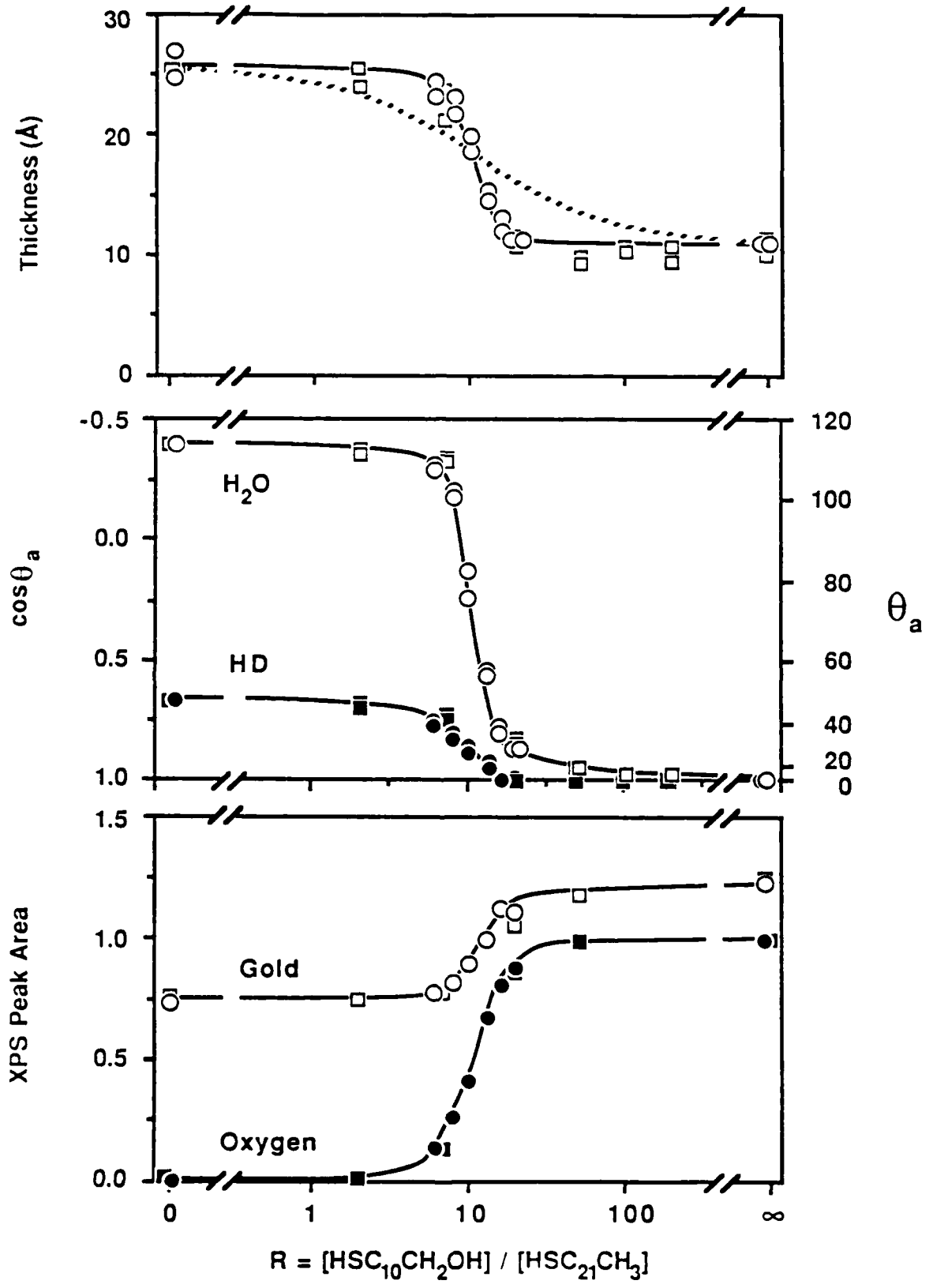
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R = [HSC10CH2OH] / [HSC21CH3]

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